# Suppression of dioxin emission in incineration of poly(vinyl chloride) (PVC) as hybridized with titanium dioxide (TiO$_2$) nanoparticles

Sung Ho Kim, Seong-Yong Ahn, Seung-Yeop Kwak *

*Hyperstructured Organic Materials Research Center (HOMRC) and Department of Materials Science and Engineering, Seoul National University, San 56-1, Sillim-dong, Gwanak-gu, Seoul 151-744, Republic of Korea*

## Abstract

The present paper has demonstrated suppression of dioxin emission from poly(vinyl chloride) (PVC)/titanium dioxide (TiO$_2$) nanohybrids. In our previous paper, we suggested a novel idea for the preparation of PVC/TiO$_2$ nanohybrid through TiO$_2$ nanoparticle-integrated hyperbranched poly($\varepsilon$-caprolactone) (HPCL-TiO$_2$), aiming at a breakthrough to solve the unresolved problem in the conventional PVC/TiO$_2$ composites related to the poor dispersion of TiO$_2$ nanoparticles in PVC polymer. The integration of TiO$_2$ nanoparticles onto the HPCL could be successfully carried out by a dip-coating method based on the spontaneous self-assembly between TiO$_2$ and HPCL. In this study, three kinds of hyperbranched poly($\varepsilon$-caprolactone)s (H$_n$PCLs) were prepared by varying the number, $n$, of monomeric units on the branched backbone chains. Thereby, it was possible to control the numbers of functional ends and the contents of TiO$_2$ in the H$_n$PCL-TiO$_2$. The loadings of TiO$_2$ in the H$_n$PCL-TiO$_2$s were found to be 4.37, 3.26, and 2.93 wt% for $n$ of 5, 10, and 20, respectively. The preparation of PVC/H$_n$PCL-TiO$_2$ (60/40) blends was performed through solution blending of H$_n$PCL-TiO$_2$ with PVC in tetrahydrofurane (THF) as solvent, and the dispersities of TiO$_2$ in the resulting nanohybrids were investigated by field-emission scanning electron microscope (FE-SEM) equipped with energy dispersive spectroscopy (EDS). The FE-SEM/EDS results showed that TiO$_2$ nanoparticles were dispersed well in PVC matrix, while some agglomerates of TiO$_2$ was observed in the PVC + TiO$_2$ sample prepared from the solution blending of PVC with the same amount of TiO$_2$. The incineration experiments were performed by using a temperature-controllable electric furnace at 350 °C under the flow of ambient air, and the exhaust gases resulting from the incineration process were collected. Prior to the identification of the components emitted in the incineration process, the GC experiments for calibration were performed on several commercial standards of dioxin and organic compounds known to be dioxin precursors. The GC results on the exhaust gases from the incineration of samples showed that the emissions of dioxin and precursors were largely suppressed with the increasing content of TiO$_2$ in PVC/H$_n$PCL-TiO$_2$, i.e., the order of PVC/H$_5$PCL-TiO$_2$ > PVC/H$_{10}$PCL-TiO$_2$ > PVC/H$_{20}$PCL-TiO$_2$, as compared with those in the neat PVC/H$_n$PCL without TiO$_2$. Especially, the PVC/H$_5$PCL-TiO$_2$ with a maximum TiO$_2$ loading of 1.6 wt% showed removal efficiencies of *ca.* 60% up to 70% over the dioxin and dioxin precursors, which is equivalent to one and half to several times as much as the PVC + TiO$_2$ samples prepared through the conventional route. The remarkable enhancement of the suppression of dioxin emission in the PVC/H$_n$PCL-TiO$_2$ might be attributed to the improvement of the degree of TiO$_2$ dispersion in the nanohybrid.
© 2007 Elsevier B.V. All rights reserved.

*Keywords:* Poly(vinyl chloride) (PVC); Titanium dioxide; Nanohybrid; Dioxins; Incineration

## 1. Introduction

Poly(vinyl chloride) (PVC) has been widely used in many applications, and the worldwide demand for PVC is still growing because of its good price/performance balance [1]. A large amount of PVC raises public concern about how the wastes should be disposed [2–4]. The waste management has mainly depended on land-filling or incineration. However, due to the high population density, limited land-fill area, high costs, etc., the waste handling policy has shifted from land-filling to incineration [5]. Despite the fact that the incineration has the advantages of the reduced land usage, a high degree of destruction, and the potential for energy recovery, the incineration of PVC could cause serious environmental problems such as the emission of dioxin from inadequate equipment or inappropriate incineration [6].

* Corresponding author. Tel.: +82 2 880 8365; fax: +82 2 885 1748.
E-mail address: sykwak@snu.ac.kr (S.-Y. Kwak).

Dioxin is a general term for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), which consist of two aromatic rings that are covalently linked together by two oxygen bridges for PCDDs, or by one oxygen-bridge and a carbon–carbon bond for PCDFs [7]. The dangerous aspect of dioxin first became known to a public after the Vietnam War, and the World Health Organization (WHO) has stressed the dangerous effect of dioxin and has regulated it as a carcinogenic material. According to a number of studies addressing the mechanism of PCDD and PCDF formation, the combustion or incineration of waste materials is regarded as main causes of dioxin emission. Dioxin is known to be easily formed from the incomplete combustion of wastes or in the cooler zones of incinerators at a relatively low temperature region of 250–450 °C [8,9]. Thus, various efforts have been put in to reduce the generation of toxic chemicals, mainly by maintaining optimum combustion state and/or establishing new air pollution facility [10,11]. It has been reported that the generation of dioxins can be largely reduced by burning PVC waste in a large-scale industrial incinerator at temperatures higher than 800 °C. However, it is very difficult to completely suppress the emission of dioxin from the incineration process because of the complexities of waste sources. There are also many unmanageable sources such as trash burning of waste plastic in the field or backyard. Thus, the development of novel materials with a capability to suppress dioxin emission is expected to be a crucial complementary solution to resolve the dioxin problems.

Titanium dioxide ($TiO_2$) nanoparticles can be used as either a photocatalyst or a chemical catalyst. $TiO_2$ photocatalysis is known to generate active oxygen species, e.g. $O_2^-$, $HO_2^{\bullet}$, $HO^{\bullet}$, from $H_2O$ or $O_2$ by oxidative or reductive reactions under UV [12]. These active oxygen species lead to the degradation reaction of various chemicals and polymers. The chemical catalysis by $TiO_2$ and $TiO_2$-supported metal oxides has also been used to suppress the emission of dioxin and its precursor through the adsorption of toxic organic compounds followed by the catalytic decomposition [13–15]. In recent years, it was shown that the mixture of PVC with $TiO_2$ suppressed the emission of toxic chemicals during and after combustion of the PVC wastes [16]. Although the possibility of applying $TiO_2$ to suppress the dioxin at low temperature has been discussed in the study, there still remain some unresolved problems related to the uniform dispersion of catalyst nanoparticles in polymer matrix. The low dispersity due to the agglomeration of $TiO_2$ implies diminution of surface area of $TiO_2$ nanoparticles, which inevitably results in the degradation of the catalytic activity during the incineration.

$TiO_2$ nanoparticles can be used as either a photocatalyst or a chemical catalyst. The previous work reported the preparation of PVC/HPCL-$TiO_2$ nanohybrid and its photocatalytic degradation under UV light irradiation [17]. The fabrication of PVC/HPCL-$TiO_2$ nanohybrid was carried out by two steps through (i) the preparation of HPCL-$TiO_2$ using the self-assembly method based on the spontaneous adsorption property between $TiO_2$ and polymer [18] and subsequent (ii) solution blending of HPCL-$TiO_2$ with PVC (PVC/HPCL-$TiO_2$). The remarkable

photocatalytic degradation of PVC/HPCL-$TiO_2$ under UV irradiation was observed due to the enhancement of $TiO_2$ dispersity, as compared with the conventional PVC/$TiO_2$ mixture with similar content of $TiO_2$.

Here, we prepare three PVC/$H_n$PCL-$TiO_2$s with a variation the content of $TiO_2$ focusing on their chemical catalytic effect to decompose dioxin and organic compounds emitted from the incineration of the nanohybrid. We control the loading of $TiO_2$ in the PVC/$H_n$PCL-$TiO_2$ using $H_n$PCLs with a different number of functional end groups. From incineration experiments of PVC/$H_n$PCL-$TiO_2$, we investigate the effect of the concentration and dispersity of $TiO_2$ in PVC on the emission of dioxins. Finally, we are able to prove that the PVC/$TiO_2$ nanohybrid an eco-friendly materials could be applied for an interesting complementary approach to solve the problem of dioxin emission.

## 2. Experimental

### 2.1. Preparation of $TiO_2$ nanoparticles

$TiO_2$ nanoparticles were prepared from the controlled hydrolysis of titanium tetraisopropoxide, $Ti(OCH(CH_3)_2)_4$, in accordance with the procedures as described in the literature [19]. A 1.25 mL of $Ti(OCH(CH_3)_2)_4$ (Aldrich, 97%) dissolved in 25 mL of absolute ethanol was added to 250 mL of distilled water (4 °C) adjusted to pH 1.5 with nitric acid and vigorously stirred overnight. To obtain a powder sample, the colloidal suspension was evaporated at 35 °C using a rotavapor and dried under vacuum oven. The crystal structure of $TiO_2$ nanoparticles was characterized with a MAC Science X-ray diffractometer (MXP18X-MF22-SRA) operating in the theta–theta geometry using 18 kW Cu K$\alpha$ ($\lambda = 0.15418$ nm) radiation. The X-ray diffraction pattern showed the formation of anatase $TiO_2$, and the size of the crystallites is determined to 5.0 nm in diameter from Scherrer's formula.

Redispersing the $TiO_2$ powder in distilled water with 0.5 g of $TiO_2$/L resulted in a transparent suspension of pH 2.8 ± 0.1. The size of the $TiO_2$ particles in the colloidal solution was measured by dynamic light scattering method using a photon correlation spectroscopy system (DLS-7000, Otsuka Electric) by utilizing an Ar laser at a scattering angle of 90°. The particle size of $TiO_2$ redissolved in deionized water is 5.0 ± 1.0 nm in diameter, which is in good agreement with XRD observations. Details on experimental procedure have been described elsewhere [17].

### 2.2. $TiO_2$-integrated hyperbranched poly(ε-caprolactone) ($H_n$PCL-$TiO_2$)

Fig. 1 showed the synthesis of $H_n$PCL. By varying a ratio of initiator to monomer, we can control the number of functional end groups in the resulting $H_n$PCL without any significant change in their molecular weight. Details of the preparation and characterization of the initiator, **1**, benzyl-protected $AB_2$ macromonomer, **2**, $AB_2$ macromonomer, **3**, and hyperbranched poly(ε-caprolactone) with hydroxyl groups, **4**, were described
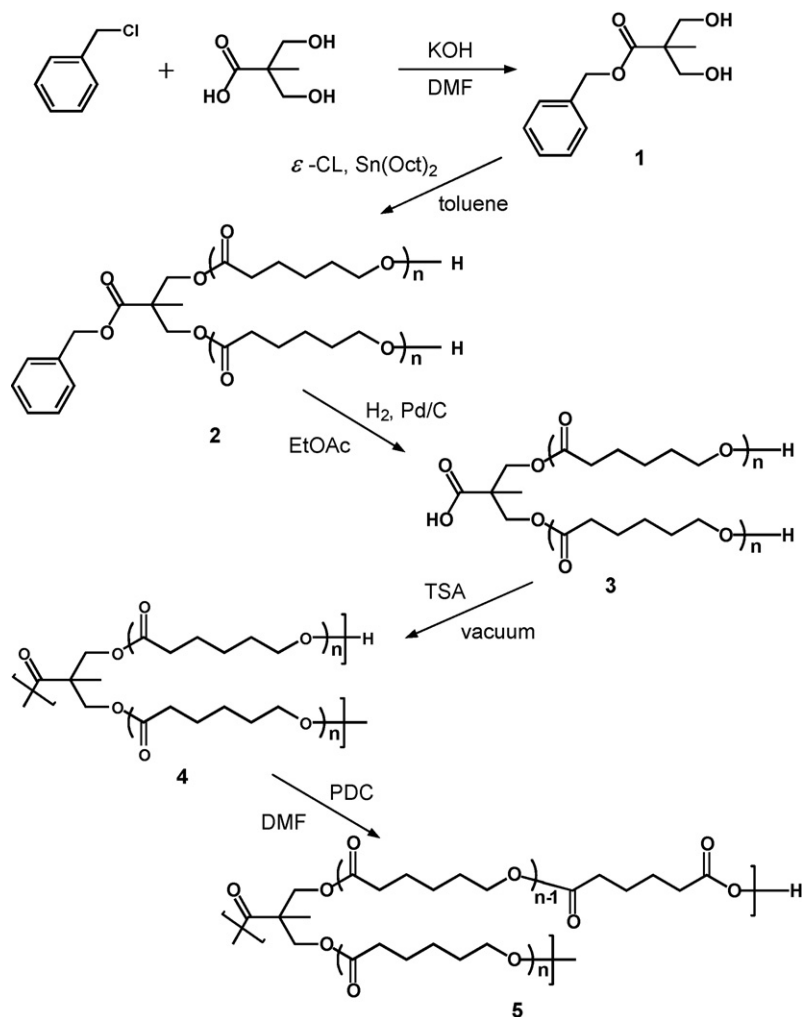
Fig. 1. Preparation scheme for $H_n$PCL.

in the previous reports [20,21]. The modification of **4** into acid derivatives, **5**, by pyridinium dichromate (PDC) oxidation reaction in dimethylformamide (DMF) was performed according to a standard procedure as the previous wok [17,22]. The reaction was confirmed by using a Bruker Avance DPX-300 $^1$H NMR spectrometer with the tetramethylsilane (TMS) signal as an internal standard in CDCl$_3$.

The incorporation of TiO$_2$ particles with $H_n$PCL was carried out by dip-coating method based on spontaneous self-assembly property between TiO$_2$ and polymer with COOH groups. Two
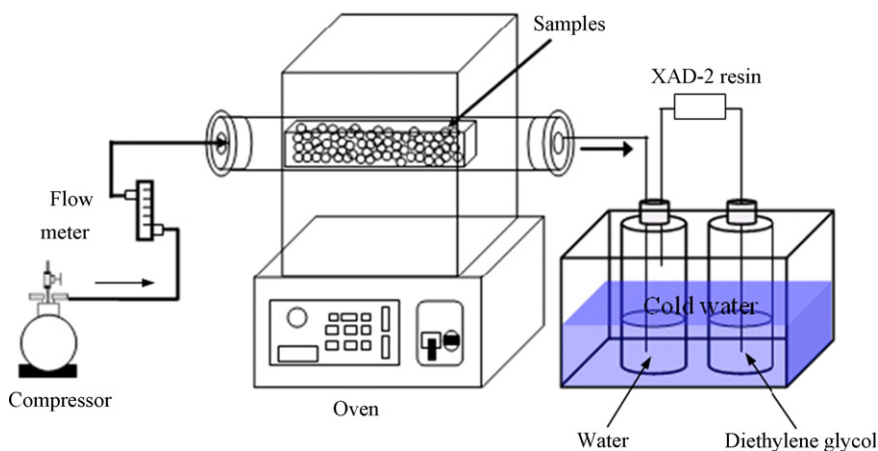


Fig. 2. Schematic representation of the apparatus for the incineration experiments.

Table 1
General characteristics for hyperbranched poly(ε-caprolactone)

| Sample | $[\varepsilon\text{-CL}]_0/[-\text{OH}]^a$ | $n^b$ | $\langle N_{AB_2} \rangle^c$ | $\langle N_{AB_2} \rangle + 1$ | $M_n/(M_n/M_w)^d$ |
|---|---|---|---|---|---|
| $H_5PCL$ | 5 | 5.7 | 8.1 | 9.1 | 11,800/1.8 |
| $H_{10}PCL$ | 10 | 10.3 | 5.1 | 6.1 | 12,600/1.6 |
| $H_{20}PCL$ | 20 | 20.1 | 3.3 | 4.3 | 15,700/1.5 |

[a] Ratio of ε-caprolactone monomer to initiating hydroxyl group.
[b] Average number of ε-caprolactone units in $AB_2$ macromonomers determined by ^{1}H NMR measurement.
[c] Number of the $AB_2$ macromonomer in HPCLs determined from ^{1}H NMR.
[d] Molecular weight and distribution obtained from SEC-MALLS.

grams of substance **5** was dipped in 1 L of the transparent $TiO_2$ colloidal solution (0.5 g $TiO_2$/1 L $H_2O$) for 3 h to deposit $TiO_2$ nanoparticles on substance **3**. Isolation of polymer from aqueous colloidal solution of $TiO_2$ was achieved by filtration to give $H_nPCL$-$TiO_2$s, which was thoroughly washed with distilled water and dried under vacuum. The $H_nPCL$-$TiO_2$ powders were characterized by thermogravimetric analysis (TGA) employing a TA Instruments TGA 2050 thermal analyzer. The temperature was increased from 30 to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere, and the residual weight at 600 °C was used to determine the contents of the inorganic nanoparticle in $H_nPCL$-$TiO_2$s.

## 2.3. Poly(vinyl chloride) (PVC)/$H_nPCL$-$TiO_2$ nanohybrid

PVC/$H_nPCL$-$TiO_2$ nanohybrids were prepared by solution blending in tetrahydrofuran (THF) as solvent at a ratio of 60:40 (w/w) to have the thickness of *ca.* 0.2 mm. The PVC used for the blends was LS-100 provided by LG Chem, Ltd., which is a general purpose suspension resin with the degree of polymerization (DP) of 1000 ± 50. The degree of dispersion
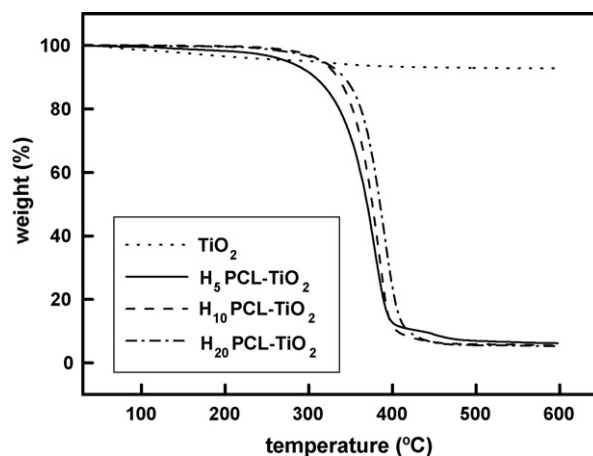


Fig. 4. TGA thermograms of $TiO_2$ and $H_nPCL$-$TiO_2$.

of $TiO_2$ in PVC/$H_nPCL$-$TiO_2$ was investigated by a JEOL JSM-6700F field-emission scanning electron microscope (FE-SEM) equipped with an energy dispersive spectrometer (EDS) that employs an exciting electron beam of 20 keV. Inca 2000 program was used to analyze the energy-dispersive spectra and obtain quantitative results. For comparison, FE-SEM/EDS analyses were also performed on PVC + $TiO_2$ sample which was prepared by solution blending of $TiO_2$ nanoparticle with PVC dissolved in THF.

## 2.4. Incineration experiment

The incineration of samples was performed with a temperature-controllable electric furnace at 350 °C under the ambient air as a carrier gas with a flow rate of *ca.* 0.85 L/min for a sampling time of *ca.* 4 h. For comparison, the masses of PVC in samples incinerated in one experiment were fixed to be equal to 18 g. For example, total masses of samples were *ca.* 30 g for PVC/$H_nPCL$-$TiO_2$ (or PVC/$H_nPCL$) and *ca.* 18 g for PVC + $TiO_2$ (or PVC), respectively. Exhaust gases emitted from the incineration of samples were collected by using XAD-2 resin and two kinds of impingers containing distilled water or diethylene glycol (Fig. 2), the simplified sampling system based on the US EPA method 23 for sampling dioxins and dioxin-like compounds contained in the flue gas. The exhaust gases from the combustion of samples were first condensed and adsorbed into 200 mL of water impinger, XAD-2 adsorbent and 300 mL of diethylene glycol impinger in a cooling box. The resin was
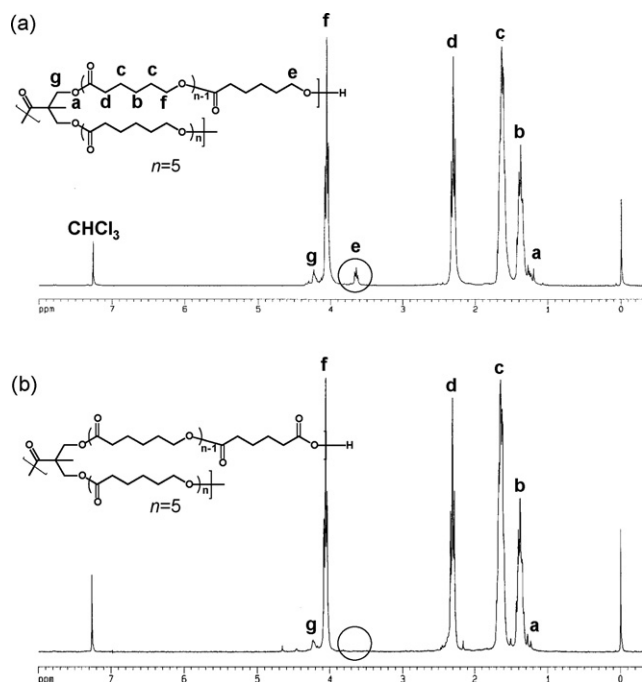


Fig. 3. [1]NMR spectra of $H_nPCLs$ before (a) and after (b) modification reaction.

Table 2
Composition ratios of the constituents and thermal degradation temperature for $H_nPCL$-$TiO_2$

| $n$ | $T_{d_{10}}^a$ | Residual weight at 600 °C (wt%) | | | Content of the constituent (wt%) | |
|---|---|---|---|---|---|---|
| | | $W_{TiO_2}$ | $W_{H_nPCL}$ | $W_{H_nPCL-TiO_2}$ | $F_{H_nPCL}$ | $F_{TiO_2}$ |
| 5 | 307.3 | | 2.25 | 6.21 | 95.63 | 4.37 |
| 10 | 334.4 | 92.80 | 2.58 | 5.52 | 96.74 | 3.26 |
| 20 | 338.7 | | 2.61 | 5.25 | 97.07 | 2.93 |

[a] Temperature of 10% weight loss by thermal degradation.

Table 3
Composition ratios for PVC/H$_n$PCL-TiO$_2$ nanohybrid

| $n$ | Contents of the constituents | | | | |
|---|---|---|---|---|---|
| | C/O/Cl/Ti[a] | PVC[b] | H$_n$PCL[b] | TiO$_2$[b] | $R$[c] |
| 5 | 72.25/11.12/16.28/0.35 | 58.0 | 40.4 (96.2) | 1.6 (3.8) | 0.87 |
| 10 | 71.38/11.04/17.32/0.26 | 61.7 | 38.2 (96.9) | 1.2 (3.1) | 0.93 |
| 20 | 72.50/11.09/16.18/0.23 | 57.7 | 41.0 (97.6) | 1.0 (2.4) | 0.81 |

[a] Atomic concentrations of elements obtained from FE-SEM/EDS analysis.
[b] Weight fractions of constituents in PVC/H$_n$PCL-TiO$_2$, and the values in the parentheses are those based on the sum of H$_n$PCL and TiO$_2$.
[c] Ratio of surface concentration of TiO$_2$ to its total loading.

Soxhlet extracted for 16 h with toluene. Then, the solution was mixed with the solutions of two impingers after the adsorption step. The probe and bottles were carefully rinsed with ethyl alcohol and toluene, and then the solvents used in the rinse were also accumulated and repeatedly extracted with 300 mL of toluene several times. The extract was stirred with a small amount of MgSO$_4$, separated through glass filter, and concentrated to approximately 50 mL by employing a rotary evaporator at a temperature of 40 °C. The condensate was cleaned up through the column packed with silica-gel 60 and Celite with eluting toluene, and evaporated one more time up to *ca.* 5 mL. Then, the sample was finally concentrated to exactly 1 mL in a water bath of 35 °C by using Kuderna–Danish (K–D) concentrator under a nitrogen gas blowing.

### 2.5. Analyses of concentrations of dioxin and precursors in concentrated solutions collected from the incineration of samples

The final concentrated solution of exhaust gases were analyzed by gas chromatography (GC) using a Hewlett Packard (HP) 6890 gas chromatograph equipped with a HP 5973 mass selective detector (MSD). The GC analyses were carried out on a DB-5 ms GC column (30 m length, 0.25 mm i.d., 0.25 μm
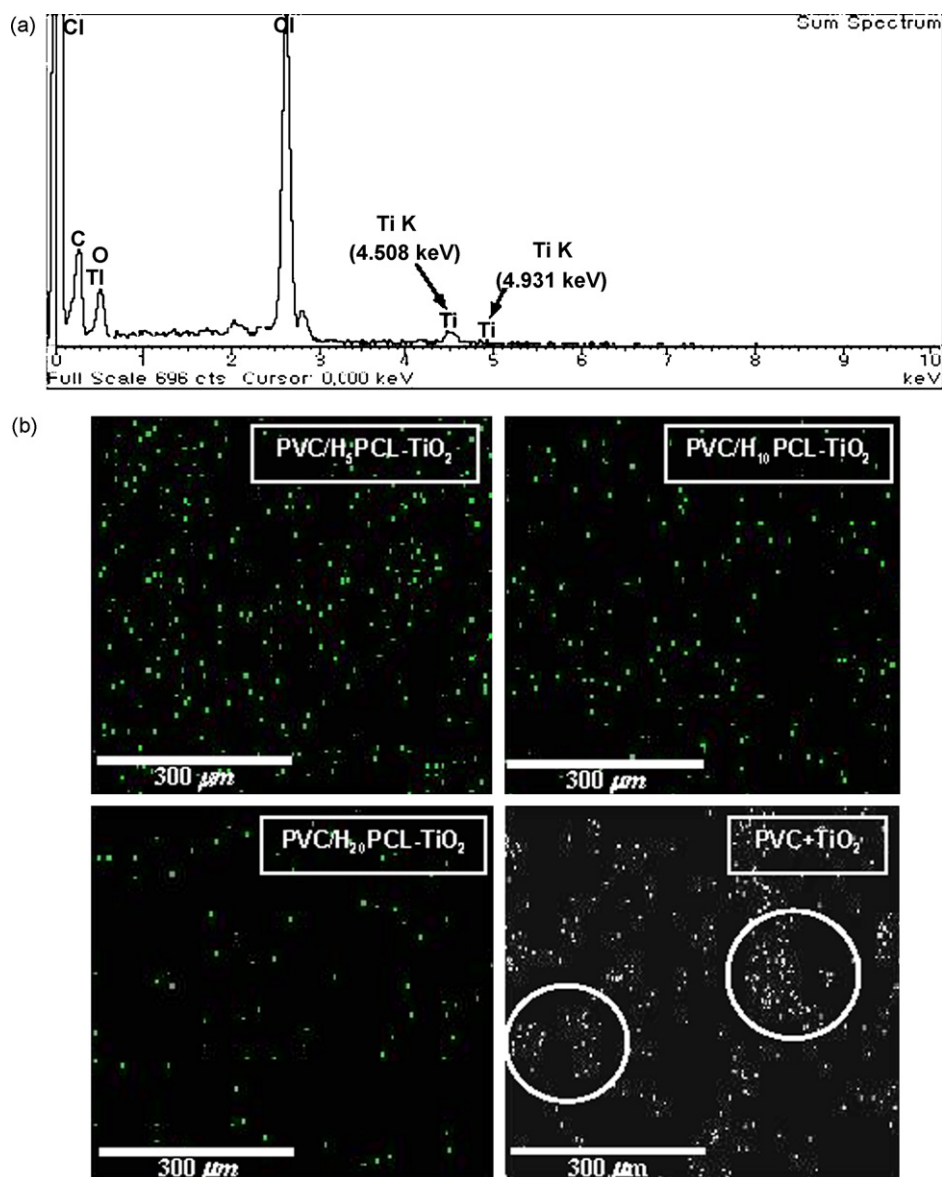


Fig. 5. Energy-dispersive X-ray spectrum (a) and FE-SEM/EDS images (b) for PVC/H$_n$PCL-TiO$_2$ and PVC + TiO$_2$.

film thickness) with the following condition: injector temperature of 250 °C, initial temperature of 90 °C for 1 min, rising by 10 °C/min to 120 °C, then 4 °C/min to 310 °C and finally held for 10 min.

Prior to the identification of the components emitted in the incineration process, the GC experiments for calibration were performed on several commercial standards, *i.e.*,

pentachlorophenol (PCPh), hexachlorobenzene (HCBz), pentachlorobenzene (PCBz), 1,2,3,4-tetrachlorobenzene (1,2,3,4-$T_4$CBz), 2,4,6-trichlorophenol (2,4,6-$T_3$CPh), and 1,2,4,5-tetrachlorobenzene (1,2,4,5-$T_4$CBz), which are reported to be the typical precursors to the dioxin formation [23–25]. In addition, a dioxin standard of 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin (2,3,7,8-$T_4$CDD, 10 µg/mL, Supelco), known as one of
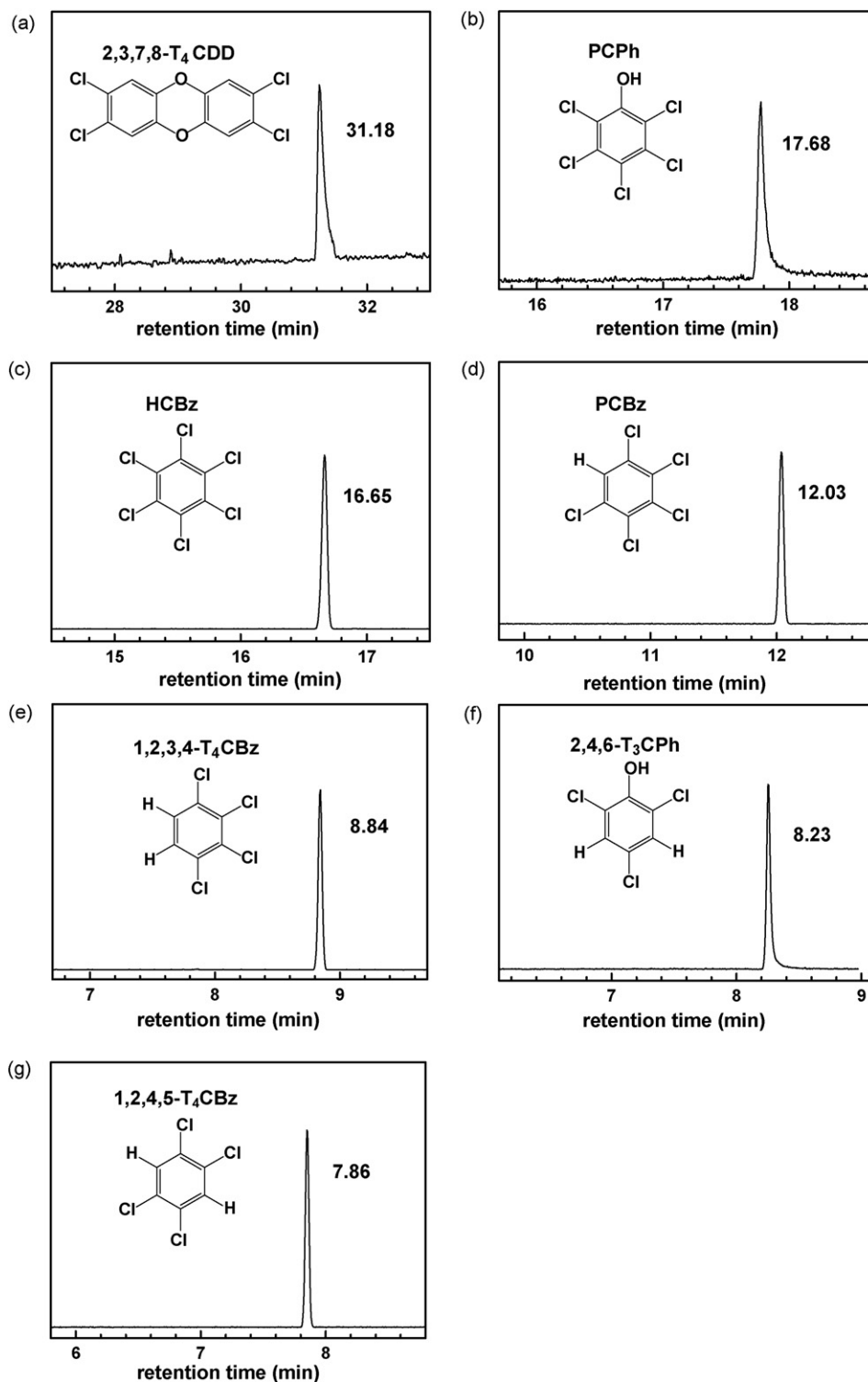


Fig. 6. Gas chromatograms for standard samples of 2,3,7,8-$T_4$CDD (a), PCPh (b), HCBz (c), PCBz (d), 1,2,3,4-$T_4$CBz (e), 2,4,6-$T_3$CPh (f), and 1,2,4,5-$T_4$CBz (g).

the most highly toxic dioxins, was also used for the calibration. The concentrations of the components in the exhaust gas were determined from the calibration curves obtained from various concentrations of the standard samples.

## 3. Results and discussion

### 3.1. TiO₂-integrated hyperbranched poly(ε-caprolactone) (HₙPCL-TiO₂)

The general procedure for the preparation of HₙPCLs with COOH functional groups is shown in Fig. 1, where the number of the functional groups has a variation with the average number of ε-caprolactone units in AB₂ macromonomers, n, as reported in our previous report (Table 1) [17,20,21]. Fig. 3 shows ¹H NMR spectra of H₅PCL before and after the modification reaction. The proton peak assigned to the ends (–CH₂–OH, 3.59 ppm) disappears, and the value of d–f increases with the conversion of –CH₂OH to –COOH. This implies that the modification reaction has been successfully performed without forming any by-product. Similar results are observed in those of H₁₀PCL and H₂₀PCL.

Fig. 4 is TGA curves of H₅PCL-TiO₂, H₁₀PCL-TiO₂, H₂₀PCL-TiO₂ and TiO₂ nanoparticle. A dramatic weight loss in the temperature range from 300 and 400 °C is observed for the HₙPCL-TiO₂s, while TiO₂ nanoparticle exhibits a slight decrease with increase in the temperature. From the TGA results, we evaluate the loading of TiO₂ in HₙPCL-TiO₂ according to the following equation:

$$W_{\text{H}_n\text{PCL-TiO}_2} = W_{\text{H}_n\text{PCL}}(1 - F_{\text{TiO}_2}) + W_{\text{TiO}_2}F_{\text{TiO}_2} \qquad (2)$$

where $W_{\text{H}_n\text{PCL-TiO}_2}$, $W_{\text{H}_n\text{PCL}}$, and $W_{\text{TiO}_2}$ are the residual weights of samples at 600 °C measured by TGA, and $F_{\text{TiO}_2}$ is the weight fraction of TiO₂ in HₙPCL-TiO₂. The values of $F_{\text{TiO}_2}$ are summarized in Table 2. This TGA result shows good agreement with the value from X-ray photoelectron spectroscopy of our previous report [17]. The TiO₂ loading increases with the increasing number of functional groups in order of H₂₀PCL-TiO₂ < H₁₀PCL-TiO₂ < H₅PCL-TiO₂. The TGA result was further used to thermal stability of HₙPCL-TiO₂ from measurement of $T_{d10}$. As listed in Table 2, thermal degradation temperatures of HₙPCL-TiO₂ are ranging from 307 to 340 °C. These values are higher than the initial thermal degradation temperatures (200–220 °C) of PVC, implying that the stability of PVC product was not deteriorated with the addition of HₙPCL-TiO₂.

### 3.2. Blend of PVC with HₙPCL-TiO₂ (PVC/HₙPCL-TiO₂)

The PVC/HₙPCL-TiO₂ (60/40) films with a variation of TiO₂ contents were prepared through solution blending process in THF as a solvent. The composition ratios for PVC/HₙPCL-TiO₂ were analyzed from the energy-dispersive X-ray energy spectra as summarized in Table 3. Considering that FE-SEM/EDS gives a surface-sensitive concentration with an effective probing depth of ca. 1 μm, the distribution of TiO₂ in PVC film

can be discussed as follows:

$$R_{\text{surface/total}} = \frac{C_{\text{TiO}_2/\text{surface}}}{C_{\text{TiO}_2/\text{total}}} \qquad (3)$$

where $R_{\text{surface/total}}$ is a ratio of surface concentration of TiO₂ to its total concentration, $C_{\text{TiO}_2/\text{surface}}$ is the concentration of TiO₂ measured from FE-SEM/EDS, and $C_{\text{TiO}_2/\text{total}}$ is the total loading of TiO₂ calculated from TGA results. If TiO₂ nanoparticles were localized in either surface or bottom of the bulk film, the $R$ value would be greater or smaller than the value of 1. Our samples show the values of 0.81–0.93, indicating relatively good dispersion of TiO₂ in the resulting PVC/TiO₂ films.

Uniform distribution of TiO₂ nanoparticles within the whole film has an important role in determining bulk properties of PVC/TiO₂ product. Thus, the distribution of TiO₂ in PVC/HₙPCL-TiO₂ film was investigated from Ti mapping image taken with 64 × 64 pixels in a projection area of ca. 600 μm × 600 μm, although individual nanoparticles cannot be shown from such a low magnification image. The Ti mapping images employing Kα peak of Ti indicates the spatial distribution of element collected and averaged at each point of the surface. The PVC/HₙPCL-TiO₂ shows uniform distribution of Ti spots while we can easily see localized ones in the image of PVC + TiO₂ sample (Fig. 5). The combined consideration of a TiO₂ surface content with mapping image results verified the enhancement in the dispersion of TiO₂ in PVC/HₙPCL-TiO₂ nanohybrids.

### 3.3. GC analyses for standard samples

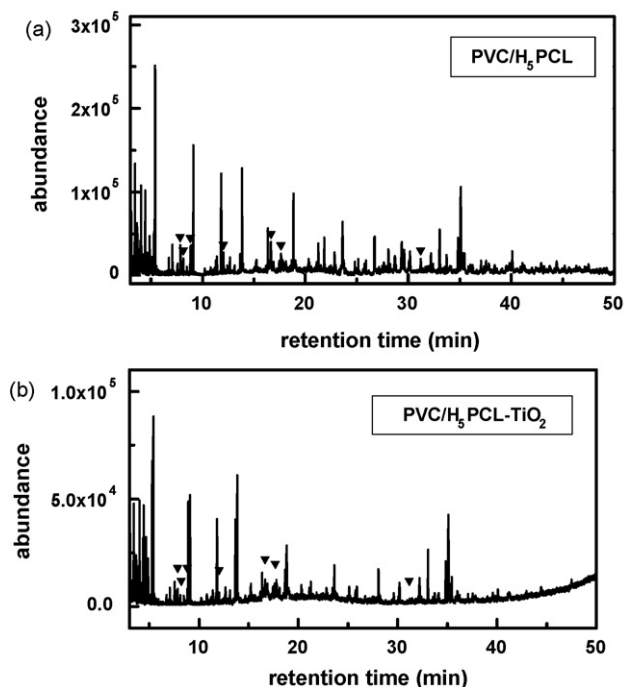The chlorobenzenes (CBz) and chlorophenols (CPh) investigated in this study are regarded as the principal



Fig. 7. Typical gas chromatograms of concentrated solutions collected from the incineration of PVC/HₙPCL (n = 5) (a) and PVC/HₙPCL-TiO₂ (n = 5) (b).

precursors to form the polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo-p-furans (PCDF) during the incineration process [23–25]. The 2,3,7,8-T$_4$CDD is one of toxic dioxin congeners the most widely studied as a model dioxin compound. Fig. 6 illustrates the gas chromatograms for the standard samples: the retention times of 31.18, 17.68, 16.65,

12.03, 8.84, 8.23, 7.86 min for 2,3,7,8-T$_4$CDD, PCPh, HCBz, PCBz, 1,2,3,4-T$_4$CBz, 2,4,6-T$_3$CPh, and 1,2,4,5-T$_4$CBz, respectively. The characteristic values of retention time and peak area with a variation on the concentration of samples would be used for identification and calibration of gas components emitted from further incineration experiments.
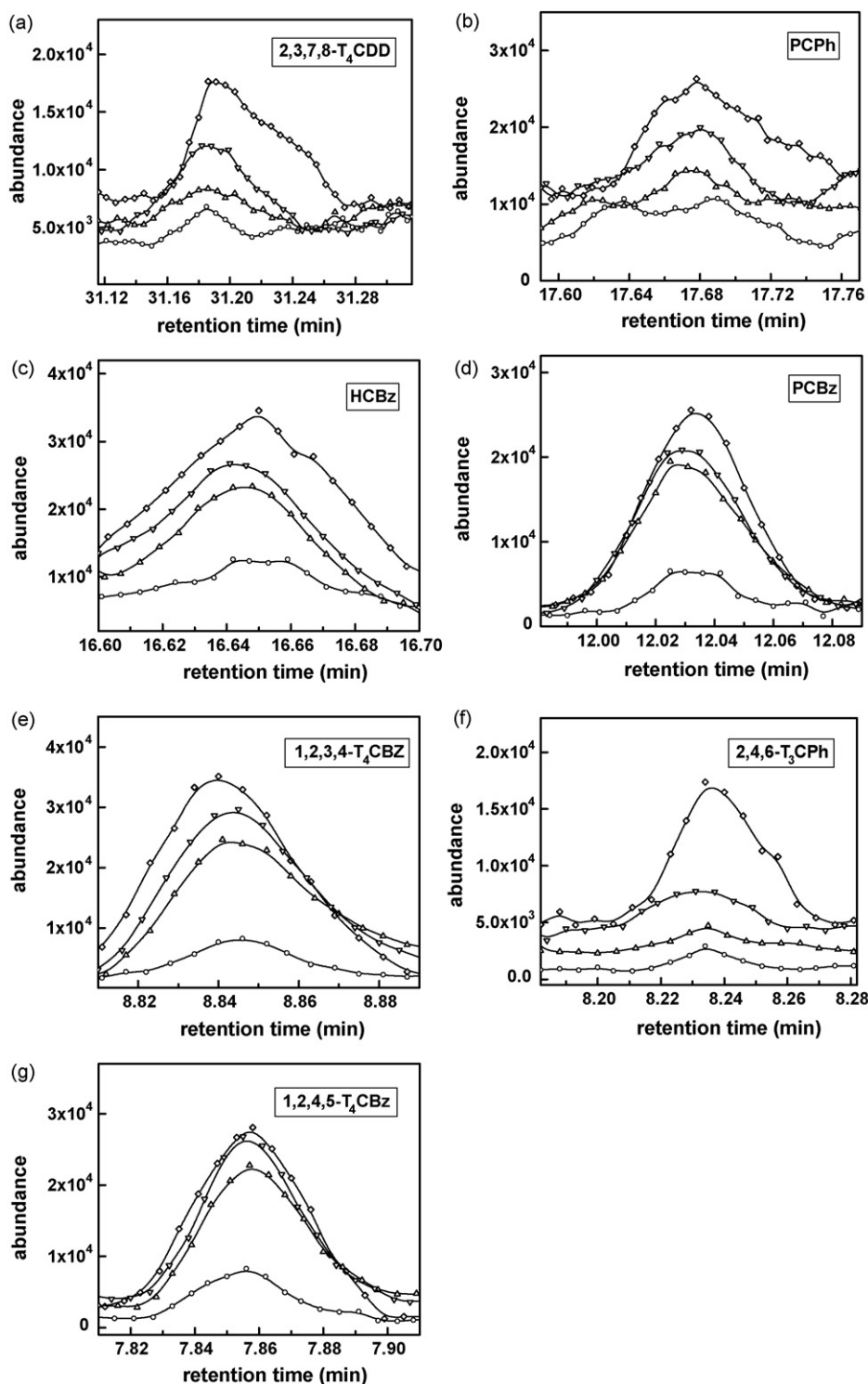


Fig. 8. Enlarged gas chromatograms for PVC/H$_5$PCL ($\diamond$), PVC/H$_{20}$PCL-TiO$_2$ ($\triangledown$), PVC/H$_{10}$PCL-TiO$_2$ ($\triangle$), and PVC/H$_5$PCL-TiO$_2$ ($\bigcirc$): 2,3,7,8-T$_4$CDD (a), PCPh (b), HCBz (c), PCBz (d), 1,2,3,4-T$_4$CBz (e), 2,4,6-T$_3$CPh (f), and 1,2,4,5-T$_4$CBz (g).

Table 4
Concentrations of dioxin and precursors in concentrated solution collected from the incineration of PVC and PVC/TiO$_2$ nanohybrids

| Sample | Concentration (ppm)/removal efficiency (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 2,3,7,8-T$_4$CDD[a] | PCPh[b] | HCBz[c] | PCBz[d] | 1,2,3,4-T$_4$CBz[e] | 2,4,6-T$_3$CPh[f] | 1,2,4,5-T$_4$CBz[g] |
| PVC/H$_5$PCL-TiO$_2$ | 1.58/68.1 | 3.84/61.4 | 6.87/60.9 | 3.25/65.0 | 3.62/73.0 | 2.04/74.2 | 1.93/73.5 |
| (PVC/H$_5$PCL) | (4.95) | (9.96) | (17.57) | (9.28) | (13.39) | (7.93) | (7.28) |
| PVC/H$_{10}$PCL-TiO$_2$ | 3.13/35.7 | 7.69/29.3 | 11.07/35.8 | 7.51/23.1 | 10.18/23.1 | 5.06/31.4 | 4.98/32.6 |
| (PVC/H$_{10}$PCL) | (4.87) | (10.88) | (17.25) | (9.76) | (13.24) | (7.37) | (7.39) |
| PVC/H$_{20}$PCL-TiO$_2$ | 4.59/6.9 | 8.88/16.9 | 13.63/19.9 | 8.16/19.1 | 11.33/16.3 | 6.13/19.6 | 5.88/18.7 |
| (PVC/H$_{20}$PCL) | (4.93) | (10.69) | (17.02) | (10.08) | (13.53) | (7.63) | (7.23) |
| PVC + TiO$_2$ | 8.07/47.5 | 50.23/19.8 | 34.36/15.9 | 32.25/36.3 | 40.36/37.3 | 21.57/50.2 | 14.84/9.1 |
| (PVC) | (15.38) | (62.65) | (40.88) | (50.65) | (64.33) | (43.35) | (16.33) |

[a] 2,3,7,8-Tetrachloro-dibenzo-p-dioxin.
[b] Pentachlorophenol.
[c] Hexachlorobenzene.
[d] Pentachlorobenzene.
[e] 1,2,3,4-Tetrachlorobenzene.
[f] 2,4,6-Trichlorophenol.
[g] 1,2,4,5-Tetrachlorobenzene.

## 3.4. Concentrations of dioxin and precursors in the concentrated solution

Fig. 7 shows the typical gas chromatograms of concentrated solutions collected from the incineration of PVC/H$_n$PCL and PVC/H$_n$PCL-TiO$_2$. Complexity of exhaust gases emitted from the incineration of PVC compounds makes it very difficult to exactly identify the whole of by-products from incineration process. The formation of CO$_2$ and some incomplete combustion products such as CO has been reported in the literature for the oxidation of polychlorinated compounds [26–28]. From a practical standpoint, the formation of CO or any other partial oxidation by-product is regarded as not representing a problem due to the very low concentration of PCDD/PCDFs in the flue gas of the incinerator and their extremely high toxicity equivalence of dioxin [26]. Judging from the values of the ordinate indicative of the abundance of the specific compounds, it can be easily seen that the amount of gas emission is largely reduced in the incineration of PVC/H$_n$PCL-TiO$_2$, compared with that of PVC/H$_n$PCL. Because of the extremely high toxicity of dioxin, the GC analyses were performed on toxic 2,3,7,8-T$_4$CDD dioxin and the dioxin precursors.

The specific regions for the toxic dioxin and its precursors mentioned above are enlarged as shown in Fig. 8. This figure shows that their emissions are largely suppressed with increasing the contents of TiO$_2$ in PVC/H$_n$PCL-TiO$_2$, i.e., the order of PVC/H$_5$PCL-TiO$_2$ > PVC/H$_{10}$PCL-TiO$_2$ > PVC/H$_{20}$PCL-TiO$_2$. For the PVC/H$_5$PCL-TiO$_2$ nanohybrid, the peak of 2,3,7,8-T$_4$CDD in Fig. 8(a) is decreased to ca. 30% of that of the PVC/H$_5$PCL without TiO$_2$. As seen in Fig. 8(b)–(g), the emissions of organic compounds, also known as dioxin precursors, are vigorously reduced in the PVC/H$_n$PCL-TiO$_2$ nanohybrids. Based on the calibration using standard samples, the concentrations of the components in the final concentrated solutions are determined and used for the calculation of the removal efficiencies of the PVC/H$_n$PCL-TiO$_2$ over the neat PVC/H$_n$PCL. The removal efficiency of dioxin and its

precursors can be calculated from the following equation:

$$E_{removal} (\%) = \left( 1 - \frac{C_{PVC/H_nPCL-TiO_2}}{C_{PVC/H_nPCL}} \right) \times 100 \qquad (3)$$

where $E_{removal}$ is the removal efficiency of PVC/H$_n$PCL-TiO$_2$ over PVC/H$_n$PCL for the selected dioxin or precursor components, and $C_{PVC/H_nPCL-TiO_2}$ and $C_{PVC/H_nPCL}$ are the concentrations of the components in the concentrated solution collected from the incineration of PVC/HPCL-TiO$_2$ and PVC/HPCL, respectively, as summarized in Table 4. The PVC/H$_5$PCL-TiO$_2$ shows the removal efficiencies of ca. 60% up to 70% over the dioxin and precursor compounds investigated in this study. For comparison, the incineration experiment was also performed on PVC + TiO$_2$ sample prepared by the solution-blending of PVC with the same amount of TiO$_2$ as the PVC/H$_5$PCL-TiO$_2$. In the PVC + TiO$_2$ sample, the emission of toxic organic compounds is also reduced to some extent, but its removal efficiencies are inferior to that of PVC/H$_5$PCL-TiO$_2$. The PVC/H$_5$PCL-TiO$_2$ shows the enhancement in the capability to suppress the toxic dioxin and organic compounds from one and half to several times as much as the PVC + TiO$_2$. Considering that they were prepared by the same conditions, i.e., the type and amount of TiO$_2$ and mass of PVC except the degree of dispersion of the nanoparticles in the polymer matrix, the remarkable difference between PVC/H$_5$PCL-TiO$_2$ and PVC + TiO$_2$ might be attributed to the enhanced dispersity of TiO$_2$ in the former as confirmed with the microscopic images.

Catalytic activity of polymer/catalyst composite could be improved by (i) development of new catalyst and (ii) good dispersion of catalyst in polymer matrix. This study can be understood as a model study focusing on the importance of the dispersion of nanosized catalyst in the functional nanocomposites. Although many researchers confirmed that pure TiO$_2$ exhibits some activity for the oxidation of several Cl-containing organic compounds such as methylene chloride and 1,2-dichlorobenzene, the addition of a second transition metal oxide significantly enhances the activity of the catalysts

[26–28]. Further improvement in removal efficiency of toxic compounds could be achieved by using more effective catalysts, such as $TiO_2$-supported transition metal or oxide ones. The work using highly efficient $TiO_2$-based catalyst will be treated in a publication soon.

## 4. Conclusions

In this study, we investigated the emissions of dioxin and dioxin precursors from the incineration of PVC/$H_n$PCL-$TiO_2$ and compared with those from the incineration of PVC/$H_n$PCL without $TiO_2$ and/or the conventional PVC + $TiO_2$ composite.

(1) Three kinds of $H_n$PCLs with a different number of functional ends were used for the preparation of $H_n$PCL-$TiO_2$s, which were blended with PVC to form PVC/$H_n$PCL-$TiO_2$s with a different concentration of $TiO_2$, *i.e.*, 1.6, 1.2, and 1.0 wt% for $n$ of 5, 10, and 20, respectively. The spectroscopic observations showed that the PVC/$H_n$PCL-$TiO_2$ films were successfully prepared without causing the formation of $TiO_2$ agglomerates in the films.
(2) The incineration experiments were performed with a temperature-controllable electric furnace at 350 °C under the flow of ambient air, and the exhaust gases were collected and analyzed by gas chromatography. The emissions of dioxin and precursors were largely suppressed with the increasing contents of $TiO_2$ in PVC/$H_n$PCL-$TiO_2$s. The PVC/$H_5$PCL-$TiO_2$ with a maximum $TiO_2$ loading of 1.6 wt% showed removal efficiencies of *ca.* 60% up to 70% over the dioxin and precursors, which is equivalent to one and half up to several times as much as the PVC + $TiO_2$ prepared from the similar contents of PVC and $TiO_2$.

## Acknowledgement

## References

[1] H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges, J.I. Kroschwitz, Encyclopedia of Polymer Science and Engineering, John Wiley & Sons, New York, 1985.
[2] Y. Saeki, T. Emura, Prog. Polym. Sci. 27 (2002) 2055–2131.
[3] S.S. Hill, B.R. Shaw, A.H.B. Wu, Clin. Chem. Acta 304 (2001) 1–8.
[4] L.L. Forestier, G. Libourel, Environ. Sci. Technol. 32 (1998) 2250–2256.
[5] K.-J. Shin, Y.-S. Chang, Chemosphere 38 (1999) 2655–2666.
[6] A.A. Meharg, R.F. Shore, M.C. French, D. Osborn, Environ. Pollut. 97 (1997) 213–220.
[7] J.J. Spivey, J.B. Butt, Catal. Today 11 (1992) 465–500.
[8] H. Hagenmaier, M. Kraft, H. Brunner, R. Haag, Environ. Sci. Technol. 21 (1987) 1080–1084.
[9] J. Hahn, C. Nagge, P. Pohlot, B. Bahor, D. Sussman, Chemosphere 25 (1992) 153–156.
[10] K. Rachunathan, B.K. Gullett, Environ. Sci. Technol. 30 (1996) 1827–1834.
[11] S. Horikoshi, N. Serpon, Y. Hisamatsu, H. Hidaka, Environ. Sci. Technol. 32 (1998) 4010–4016.
[12] H. Hidaka, Y. Suzuki, K. Nohara, S. Horikoshi, Y. Hisamatsu, E. Pelizzetti, N. Serpone, J. Polym. Sci. A: Polym. Chem. 34 (1996) 1311–1316.
[13] F. Bertinchamps, C. Gregoire, E.M. Gaigneaux, Appl. Catal. B: Environ. 66 (2006) 1–9.
[14] R. Weber, T. Sakurai, H. Hagenmaier, Appl. Catal. B: Environ. 20 (1999) 249–256.
[15] Y. Ukisu, T. Miyadera, Appl. Catal. B: Environ. 40 (2003) 141–149.
[16] R.D. Sun, T. Nishikawa, A. Nakajima, T. Watanabe, K. Hashimoto, Polym. Degrad. Stab. 78 (2002) 479–484.
[17] S.H. Kim, S.-Y. Kwak, T. Suzuki, Polymer 47 (2006) 3005–3016.
[18] S.J. Lee, S.W. Han, M. Yoon, K. Kim, Vib. Spectrosc. 24 (2000) 265–275.
[19] W. Choi, A. Termin, M.R. Hoffmann, J. Phys. Chem. 98 (1994) 13669–13679.
[20] J. Choi, S.-Y. Kwak, Macromolecules 36 (2003) 8630–8637.
[21] J. Choi, S.-Y. Kwak, Macromolecules 37 (2004) 3745–3754.
[22] E.J. Corey, G. Schmit, Tetrahedron Lett. 20 (1979) 399–402.
[23] F.W. Karasek, L.C. Dickson, Science 237 (1987) 754–756.
[24] R. Luijk, D.M. Akkerman, P. Slot, K. Olie, F. Kapteijn, Environ. Sci. Technol. 28 (1994) 312–321.
[25] S.B. Ghorishi, E.R. Altwicker, Environ. Sci. Technol. 29 (1995) 1156–1162.
[26] S. Krishnamoorthy, J.A. Rivas, M.D. Amiridis, J. Catal. 193 (2000) 264–272.
[27] S. Krishnamoorthy, J.P. Baker, M.D. Amiridis, Catal. Today 40 (1998) 39–46.
[28] X.-Z. Jiang, L.-Q. Zhang, X.-H. Wu, L. Zheng, Appl. Catal. B: Environ. 9 (1996) 229–237.